

Numerical simulations of liquids with amorphous boundary conditions

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Abstract. It has recently become clear that simulations under amorphous boundary conditions (ABCs) can provide valuable information on the dynamics and thermodynamics of disordered systems with no obvious ordered parameter. In particular, they allow to detect a correlation length that is not measurable with standard correlation functions. Here we explain what exactly is meant by ABCs, discuss their relation with point-to-set correlations and briefly describe some recent results obtained with this technique.

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1. Introduction

Systems that can be studied with numerical simulation are rather small. Even those that can be considered “very large” by numerical simulation standards are still quite small compared to macroscopic experimental systems. Accordingly, a rather large fraction of the particles is near the boundaries, with the consequence that boundary conditions (BCs) have a significant effect on simulation results [1]. Very often, periodic boundary conditions (PBCs) are used. These conditions avoid surface effects (although of course finite-size effects are still present) and are generally the most satisfactory way of studying bulk properties of macroscopic systems [1].

Here we discuss a different kind of BCs, *amorphous boundary conditions (ABCs)*, which, as has recently become clear, are highly useful in the study of *bulk* supercooled liquids [2, 3, 4] and likely other systems where it is hard to detect spatial correlations due to lack of an obvious order parameter.

The basic idea, which is to investigate how far the effect of the BCs penetrates into the bulk, has deep roots in statistical mechanics. In fact, thermodynamic phase transitions can be characterised as points where this penetration length is infinite, and the BCs can be used to select one of several ergodic components (coexisting phases)

[5]. However this approach is not normally used in simulations, as standard correlation functions or fluctuations involving the order parameter are more convenient. In systems like supercooled liquids, however, it is not clear how to detect growing order. The novel idea [2] is to study the liquid under boundary conditions chosen by the system itself (in a sense that will become clear in sec. 2).

We discuss ABCs and discuss their close connection with point-to-set correlations [6, 7] in sec. 2. We then comment some recent numerical results on the statics (sec. 3) and dynamics (sec. 4) of liquids obtained with ABC. In sec. 5 we conclude.

2. Amorphous boundary conditions and point-to-set correlations

It will be convenient to treat first the case of lattice systems (let us call the lattice variables “spins”), and to deal with the continuum case afterwards. Consider an infinite system and chose a region \mathcal{R} of typical size R , which we shall call the cavity. Its precise shape is not important, but it must be bounded; we shall usually think of it as a sphere of radius R . We call $\sigma = \{\sigma_1, \dots, \sigma_M\}$ the spins belonging to the cavity \mathcal{R} , and $\tau = \{\tau_{M+1}, \dots, \tau_N\}$ those outside. Let $H(\sigma, \tau)$ be the hamiltonian of the infinite system.

To study the system under amorphous boundary condition means to study the (thermo)dynamics of the cavity \mathcal{R} with the full hamiltonian $H(\sigma, \tau)$ but with *fixed* values of the outside spins τ , which act as a (disorderd) surface field. Naturally one has to average all observables over different configurations of the outside spins. Thus one computes what in disordered systems is usually called the quenched average, which for the case of a one-time observable A can be written

$$\overline{\langle A \rangle}_\tau = \sum_\tau w(\tau) A_\tau, \quad \langle A \rangle_\tau = \frac{1}{\mathcal{Z}_\tau} \sum_\sigma A(\sigma, \tau) e^{-\beta H(\sigma, \tau)}, \quad (1)$$

with

$$\mathcal{Z}_\tau = \sum_\sigma e^{-\beta H(\sigma, \tau)}, \quad (2)$$

and we must specify the weight $w(\tau)$. The point is that this weight is itself Boltzmann:

$$w(\tau) = \frac{1}{\mathcal{Z}} \sum_\sigma e^{-\beta H(\sigma, \tau)} = \frac{\mathcal{Z}_\tau}{\mathcal{Z}}, \quad \mathcal{Z} = \sum_{\sigma, \tau} e^{-\beta H(\sigma, \tau)}. \quad (3)$$

In this sense the system “chooses its own BCs”. The phrase is even more appropriate when one considers the way $\overline{\langle A \rangle}_\tau$ is determined in a simulation: the system is first equilibrated in a standard run, then an equilibrium configuration is chosen and A is measured in a simulation with the spins outside the cavity artificially frozen (and the process is repeated for several starting equilibrium configurations).

2.1. One-time observables

It is easy to see that ABCs do not affect the expectation value of single-time observables. The annealed (Boltzmann) average is

$$\langle A \rangle = \frac{1}{\mathcal{Z}} \sum_{\sigma, \tau} A(\sigma, \tau) e^{-\beta H(\sigma, \tau)}. \quad (4)$$

But writing the quenched average \overline{A}_τ in full we have

$$\begin{aligned}\overline{\langle A \rangle}_\tau &= \sum_\tau \frac{\mathcal{Z}_\tau}{\mathcal{Z}} \frac{1}{\mathcal{Z}_\tau} \sum_\sigma A(\sigma, \tau) e^{-\beta H(\sigma, \tau)} \\ &= \frac{1}{\mathcal{Z}} \sum_{\tau, \sigma} A(\sigma, \tau) e^{-\beta H(\sigma, \tau)} = \langle A \rangle.\end{aligned}\quad (5)$$

Thus *for one-time observables, the quenched and annealed averages are the same.* This includes in particular the energy [8], but also all non-connected n -point static correlation functions, even those involving spins inside and outside \mathcal{R} .

2.2. Free energy, time correlations and overlap

Quantities where ABCs make a difference are the free energy (as one might expect) and, of more present interest, time correlation functions.

For the free energy one straightforwardly finds

$$\begin{aligned}\overline{F}_\tau &= -\frac{1}{\beta} \sum_\tau w(\tau) \log \mathcal{Z}_\tau = -\frac{1}{\beta} \sum_\tau w(\tau) \log \mathcal{Z} w(\tau) \\ &= F - \frac{1}{\beta} \sum_\tau w(\tau) \log w(\tau).\end{aligned}\quad (6)$$

Consider now a time correlation function. In the annealed case we have

$$\begin{aligned}C(t) &= \langle A(t)B(0) \rangle \\ &= \frac{1}{\mathcal{Z}} \sum_{\sigma, \tau, \sigma', \tau'} A(\sigma, \tau) G(\sigma\tau | \sigma'\tau', t) B(\sigma', \tau') e^{-\beta H(\sigma', \tau')},\end{aligned}\quad (7)$$

where $G(x|x', t)$ is the appropriate evolution operator, or conditional probability. The corresponding fixed- τ expression is

$$C_\tau(t) = \frac{1}{\mathcal{Z}_\tau} \sum_{\sigma\sigma'} A(\sigma, \tau) G(\sigma\tau | \sigma'\tau, t) B(\sigma', \tau) e^{-\beta H(\sigma', \tau)},\quad (8)$$

and the quenched average gives

$$\begin{aligned}\overline{C}_\tau(t) &= \sum_\tau w(\tau) C_\tau(t) \\ &= \frac{1}{\mathcal{Z}} \sum_{\sigma, \sigma', \tau} A(\sigma, \tau) G(\sigma\tau | \sigma'\tau, t) B(\sigma', \tau) e^{-\beta H(\sigma', \tau)},\end{aligned}\quad (9)$$

which differs from the annealed result (7) in that it lacks the summation over τ' .

In what follows we shall be particularly interested in the case $A = B = \sigma_i$ (where σ_i is a spin at the centre of \mathcal{R}) and in the *overlap*

$$q \equiv \overline{\langle \sigma_i \rangle_\tau \langle \sigma_i \rangle_\tau} = \overline{\langle \sigma_i \rangle_\tau^2}.\quad (10)$$

The overlap is a measure of how much the ABCs restrict the movement in phase space of the spin at the centre: the higher the q (with respect to its annealed value) the higher the restrictions imposed by the boundary. It is also the asymptotic value of the spin-spin autocorrelation:

$$\begin{aligned}\overline{\langle \sigma_i(t) \sigma_i(0) \rangle}_\tau &= \frac{1}{\mathcal{Z}} \sum_{\sigma, \sigma', \tau} \sigma_i \sigma'_i G(\sigma\tau | \sigma'\tau, t) e^{-\beta H(\sigma', \tau)} \\ &\xrightarrow{t \rightarrow \infty} \overline{\langle \sigma_i \rangle_\tau \langle \sigma_i \rangle_\tau} = q.\end{aligned}\quad (11)$$

2.3. Point-to-set correlation

The point-to-set correlation function between site i and the complement of \mathcal{R} can be defined as [7]

$$C(i, \bar{\mathcal{R}}) = \langle \sigma_i f(\tau) \rangle, \quad \text{with} \quad f(\tau) = \langle \sigma_i \rangle_\tau. \quad (12)$$

Studying the value of $C(i, \bar{\mathcal{R}})$ as a function of the size R of the cavity, one can define a characteristic length ξ_s as the value of R beyond which the correlation drops below some small value. Part of the interest of point-to-set correlations is that for models with discrete variables on rather general graphs, rigorous bounds have been proved showing that growth of correlation times must be accompanied by a growth of ξ_s [7]. A divergence of correlation times implies a divergence of ξ_s even in models where standard point-to-point correlations yield correlation lengths that are always finite [7, 6]. The correlation can be written

$$\begin{aligned} C(i, \bar{\mathcal{R}}) &= \langle \sigma_i \langle \sigma_i \rangle_\tau \rangle = \frac{1}{\mathcal{Z}} \sum_{\sigma, \tau} e^{-\beta H(\sigma, \tau)} \sigma_i \frac{1}{\mathcal{Z}_\tau} \sum_{\sigma'} e^{-\beta H(\sigma', \tau)} \sigma'_i \\ &= \sum_\tau \frac{\mathcal{Z}_\tau}{\mathcal{Z}} \left[\frac{1}{\mathcal{Z}_\tau} \sum_\sigma \sigma_i e^{-\beta H(\sigma, \tau)} \right] \left[\frac{1}{\mathcal{Z}_\tau} \sum_{\sigma'} \sigma'_i e^{-\beta H(\sigma', \tau)} \right] \\ &= \overline{\langle \sigma_i \rangle_\tau^2} = q. \end{aligned} \quad (13)$$

In this form it is clear that the point-to-set correlation is equal to the overlap measured at the centre of the cavity. It is also clear that it is related to sample-to-sample fluctuations of the spin subject to ABCs, and it has the same form as the self-overlap defined for spin glasses.

2.4. The off-lattice case

To rewrite the formulae of the previous section for the case of off-lattice particles, one must introduce a hard wall enclosing the cavity [9]. The idea is that to write something like the point-to-set correlation (13) the “set” cannot be a volume to be filled with particles; it must be an actual set of particles. In other words, one must choose the set based on the *identity* of the particles, and not on the values the particles’ degrees of freedom (choosing the particles that happen to be within some particular volume is akin to building a set of lattice sites based on the value of the site’s spin) [9].

Let us then divide the particles into mobile ($\mathbf{x} = \{\mathbf{x}_1, \dots, \mathbf{x}_M\} = \{\mathbf{r}_1, \dots, \mathbf{r}_M\}$) and frozen ($\mathbf{y} = \{\mathbf{y}_1, \dots, \mathbf{y}_{N-M}\} = \{\mathbf{r}_{M+1}, \dots, \mathbf{r}_N\}$). Then the point-to-set is

$$C(0, \bar{\mathcal{R}}) = \langle \rho(0; \mathbf{x}) f(\{\mathbf{y}\}) \rangle_{\mathcal{R}}, \quad \text{with} \quad f(\mathbf{y}) = \langle \rho(0; \mathbf{x}, \mathbf{y}) \rangle_{\mathcal{R}, \mathbf{y}}, \quad (14)$$

where in our case $\rho(\mathbf{r})$ is the coarse-grained density

$$\rho(\mathbf{r}; \mathbf{x}) = \int_{v_{\mathbf{r}}} d^3 s \sum_i^M \delta(\mathbf{s} - \mathbf{x}_i), \quad (15)$$

($v_{\mathbf{r}}$ is a small volume at the centre of \mathcal{R}) and $\langle \dots \rangle_{\mathcal{R}}$ means an average with a hard wall around \mathcal{R} , i.e.

$$\begin{aligned} \langle \dots \rangle_{\mathcal{R}} &= \frac{1}{\mathcal{Z}} \int d^M \mathbf{x} d^{N-M} \mathbf{y} \dots e^{-\beta \tilde{H}(\mathbf{x}, \mathbf{y})}, \\ \tilde{H}(\mathbf{x}, \mathbf{y}) &= H(\mathbf{x}, \mathbf{y}) + \sum_i v_{\text{in}}(\mathbf{x}_i) + \sum_i v_{\text{out}}(\mathbf{y}_i), \end{aligned} \quad (16)$$

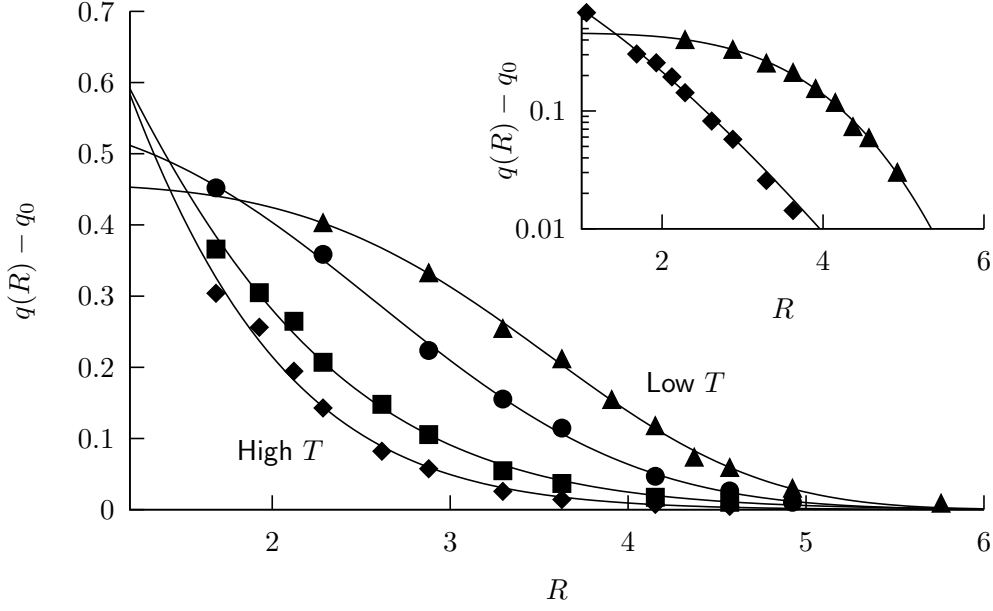


Figure 1. Point-to-set correlation (overlap) vs. cavity radius for the soft-sphere binary mixture at temperatures $T = 0.482$ (diamonds), 0.350 (squares), 0.246 (circles), and 0.203 (triangles) [4]. Lines are fits to the compressed exponential form (18). Inset: Same data for the highest and lowest temperatures in log-linear scale, showing the non-exponential character of the overlap decay at low temperatures (an exponential shows as a straight line in this plot).

where $v_{\text{in}}(\mathbf{r})$ is a potential that is 0 inside \mathcal{R} and infinite outside (and conversely for v_{out}). Then we can write the expression corresponding to (13),

$$\begin{aligned}
 C(0, \bar{\mathcal{R}}) &= \frac{1}{\bar{\mathcal{Z}}} \int d\mathbf{x} d\mathbf{y} e^{-\beta \tilde{H}(\mathbf{x}, \mathbf{y})} \rho(0; \mathbf{x}) \frac{1}{\mathcal{Z}_{\mathbf{y}}} \int d\mathbf{x}' e^{-\beta \tilde{H}(\mathbf{x}', \mathbf{y})} \rho(0; \mathbf{x}') \\
 &= \int d\mathbf{y} \frac{\mathcal{Z}_{\mathbf{y}}}{\bar{\mathcal{Z}}} \frac{1}{\mathcal{Z}_{\mathbf{y}}} \int d\mathbf{x} \rho(0; \mathbf{x}) e^{-\beta \tilde{H}(\mathbf{x}, \mathbf{y})} \frac{1}{\mathcal{Z}_{\mathbf{y}}} \int d\mathbf{x}' \rho(0; \mathbf{x}') e^{-\beta \tilde{H}(\mathbf{x}', \mathbf{y})} \\
 &= \overline{\langle \rho(0; \mathbf{x}) \rangle_{\mathbf{y}}^2}.
 \end{aligned} \tag{17}$$

3. Numerical results: statics

An off-lattice glassformer, the soft-sphere binary mixture, has been recently studied numerically under ABCs [3, 4]. In particular, the point-to-set correlation (17) was computed using Monte Carlo simulations in ref. [4]. In this work, ABCs allowed for the first time to detect a clearly growing *static* correlation length (figure 1).

Another finding of ref. [4] is that at low temperatures the decay of the overlap (or point-to-set correlation) is *non-exponential* (figure 1, inset), and can be fitted by the empirical form (compressed exponential)

$$q(R) - q_0 = A \exp \left[- (R/\xi_s)^\zeta \right], \tag{18}$$

where q_0 is the asymptotic value of the overlap.

The growth of ξ_s as temperature is decreased (and correlation times grow) is a result not unexpected (even though it took many years to develop the tools to detect

the correlation length) in the sense that it corresponds to physical intuition. As such, at the qualitative level it does not constitute a new constraint on theories of the supercooled liquid state. Instead it is the details of the τ vs. ξ_s relationship, as well as the decay of the overlap with R which are expected to provide valuable information to help discriminate among competing theories.

While the question of which theory best describes the supercooled liquid is far from settled, the numerical data on the decay of the overlap with R under ABCs have been shown to be compatible with (a slightly generalized version of) the random first-order theory (RFOT) [10, 11, 12]. According to RFOT, whether or not a region of radius R relaxes depends on the balance between the surface tension Y that develops when that region actually rearranges and the configurational entropy Σ unleashed by the rearrangement: if $Y > T\Sigma R^{d-\theta}$ (d is the dimension of the system and θ the surface tension exponent) the surface cost is larger than the entropic gain and the region does not rearrange. On the other hand, if $Y < T\Sigma R^{d-\theta}$ the entropic gain outweighs the surface energy cost and the region has a thermodynamic advantage to rearrange. The minimal rearranging size where entropy and surface tension balance, $\xi = (Y/T\Sigma)^{1/(d-\theta)}$, is the mosaic correlation length of RFOT. Introducing a distribution $P(Y)$ that allows for fluctuations of the surface tension, a decay of the overlap of the form (18) is obtained [4].

The existence of a surface energy cost required by RFOT for the situation when different states are in contact might seem in contradiction with (5), which in particular means that the energy is completely unaffected by ABCs. For a given BC, the cavity explores all possible configurations, many of which should pay a substantial energy price. Why does not this price show up in the average energy? The answer is that precisely because of this high price, those configurations are seldom visited: this is the pinning induced by the BCs, which produces a high overlap for small cavities. When the cavity is large the central region can rearrange independently of the borders and the cavity becomes ergodic; for these sizes RFOT's states are no longer well-defined. In order to detect surface tension, different *frozen* configurations must be put in contact [13, 14].

4. Numerical results: dynamics

The dynamics of a system under ABCs has been studied in refs. [15] and [16]. It is of interest to establish not only the infinite time limit of the overlap (the point-to-set value), but also how long it takes to reach the asymptotic level. This is important in two respects, and again the detailed answer is expected to provide constraints for the theories of the liquid state.

First, one asks whether the point-to-set length ξ_s is the relevant dynamic length, i.e. whether its growth actually tracks closely the growth of the correlation time τ . The rigorous bounds are rather broad: τ must grow at least linearly with ξ_s and no more than exponentially in ξ_s^d [7] (d is the space dimension). The lengthscale directly linked to τ might be another one. Another way to put the question is to ask whether ξ_s is the typical size of a cooperatively rearranging region (CRR): a CRR is a region made of particles that can only relax if they move together [17]. Thus a region larger than the size of CRRs will not relax slower than a CRR, because different regions can relax in parallel: this is thus the relevant dynamic length. Although CRRs *cannot be smaller than* ξ_s (because, by definition, regions smaller than ξ_s cannot fully relax), a region of this size could still relax differently from the bulk.

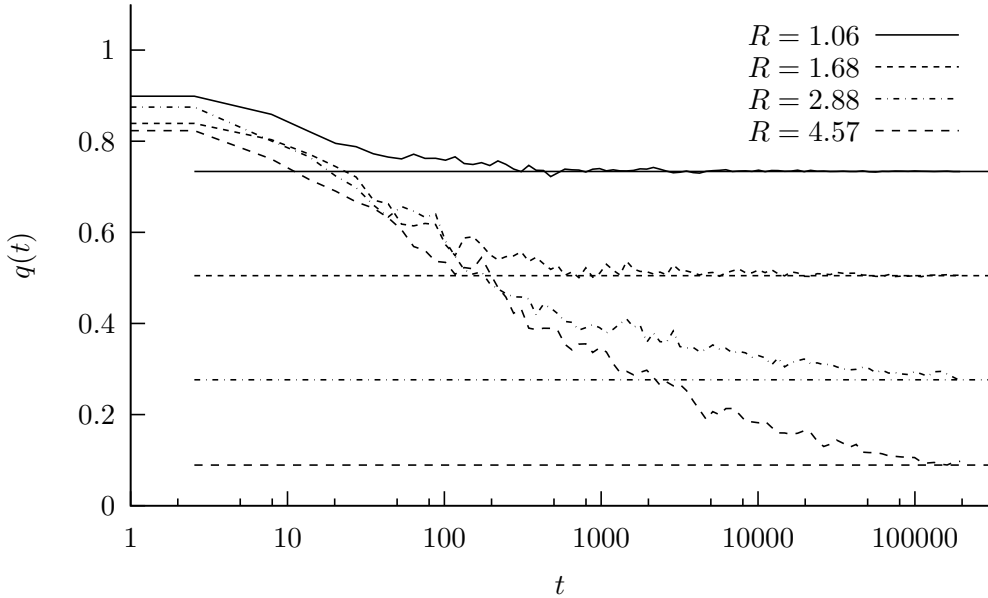


Figure 2. Time dependent overlap (see (11)) as a function of time for four cavity sizes for the soft-sphere binary mixture at $T = 0.350$ (see ref. [16]). As the point-to-set correlation (asymptotic value of $q(t)$) becomes lower, the time to reach the asymptotic value becomes larger.

The second question is whether the cavity correlation time approaches the bulk time from above or from below. Theories based on kinetic constraints, where the slowdown is ascribed to the low density of mobile regions (termed *excitations* or *defects*) [18, 19], seem to imply that the bulk equilibration time should be approached from above (*i.e.* small systems relax more slowly). On the other hand, according to RFOT the cavity equilibration time is expected to have the opposite behaviour: when frozen amorphous boundary conditions are present, small systems relax faster than large systems [20].

The (on-lattice) square plaquette model (SPM) was studied in [15]. This model's dynamics is ruled by defects, and figure 8 of ref. [15] shows clearly that the bulk correlation time is reached from *above*, while in figure 7 of the same work it can be seen that the correlation time does not reach the bulk value for the cavity size where the point-to-set correlation decays to 0 (*i.e.* ξ_s).

On the other hand, in the soft-sphere binary mixture considered in [16] the behaviour is the opposite: the correlation time grows with cavity size and approaches the bulk value from *below*, as is clear in figures 2 and 3.

Figure 3 also shows that the bulk relaxation time is reached at the point-to-set length ξ_s , *i.e.* that ξ_s is the relevant dynamic length. Thus in [16] it was concluded that ξ_s can indeed be interpreted as the typical size of CRRs.

5. Conclusions

In summary, numerical simulations with amorphous boundary conditions provide a new tool to study systems with amorphous order, such as supercooled liquids. The

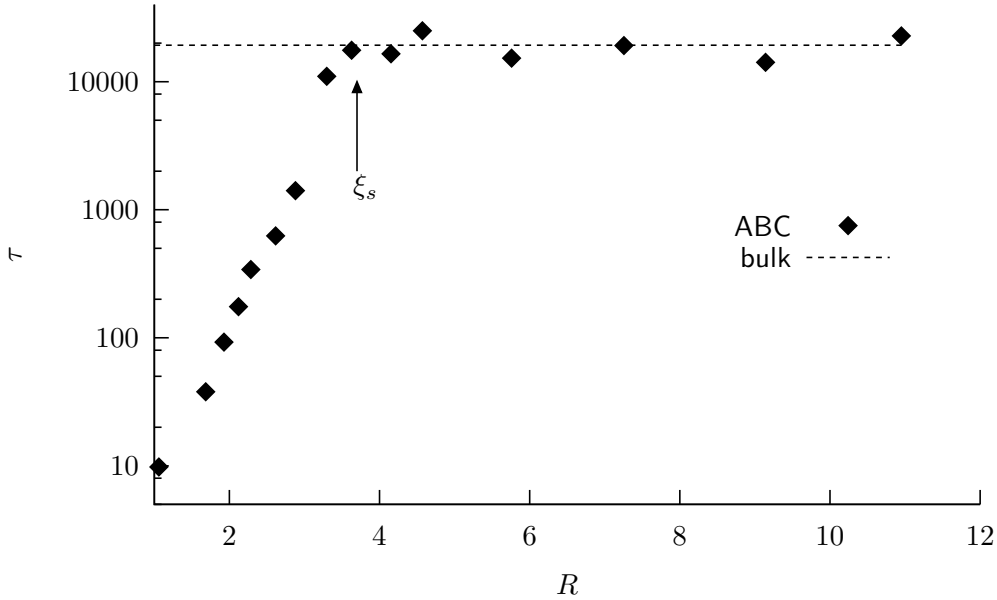


Figure 3. Cavity equilibration time vs. cavity size for the soft-sphere binary mixture at $T = 0.203$ [16]. The bulk value is reached when the cavity has the size of the static correlation length. Similar results were found for other temperatures [16].

results we have discussed here support the interpretation of ξ_s as the relevant dynamic length. This corresponds to the characteristic length ξ of the random first-order theory (RFOT) of liquids. Numerical results at low temperatures can be interpreted within an RFOT scenario which allows for surface tension fluctuations, while the correlation time that grows with R found in those studies is somewhat harder to explain in the context of defect-based theories.

However, the debate about which theory best describes supercooled liquids is not settled. We expect that numerical and theoretical exploration of situations with ABCs will provide highly valuable information and insight into the statistical mechanics of these systems, and contribute to the efforts to build a satisfactory theory.

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